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Efficacy of reactive mineral-based sorbents for phosphate, bacteria, nitrogen and TOC removal – Column experiment in recirculation batch mode

Charlotte Nilsson [a,*], Ramnath Lakshmanan [b], Gunno Renman [a,1], Gunaratna Kuttuva Rajarao [b]

[a] Department of Land and Water Resources Engineering, Royal Institute of Technology, Teknikringen 76, SE-100 44 Stockholm, Sweden

[b] School of Biotechnology, KTH Royal Institute of Technology, Roslagstullsbacken 21, SE-106 91 Stockholm, Sweden

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ABSTRACT

Two mineral-based materials (Polonite and Sorbulite) intended for filter wells in on-site wastewater treatment were compared in terms of removal of phosphate (PO_4–P), total inorganic nitrogen (TIN), total organic carbon (TOC) and faecal indicator bacteria (*Escherichia coli* and Enterococci). Using an innovative, recirculating system, septic tank effluent was pumped at a hydraulic loading rate of 3000 L m^2 d^{-1} into triplicate bench-scale columns of each material over a 90-day period. The results showed that Polonite performed better with respect to removal of PO_4–P, retaining on average 80% compared with 75% in Sorbulite. This difference was attributed to higher CaO content in Polonite and its faster dissolution. Polonite also performed better in terms of removal of bacteria because of its higher pH value. The total average reduction in *E. coli* was 60% in Polonite and 45% in Sorbulite, while for Enterococci the corresponding value was 56% in Polonite and 34% in Sorbulite. Sorbulite removed TIN more effectively, with a removal rate of 23%, while Polonite removed 11% of TIN, as well as TOC. Organic matter (measured as TOC) was accumulated in the filter materials but was also released periodically. The results showed that Sorbulite could meet the demand in removing phosphate and nitrogen with reduced microbial release from the wastewater treatment process.

1. Introduction

Water eutrophication caused by excess nutrient loading from human activities has been recognised as a major water quality issue for several decades (Conley et al., 2009). Although some environments are more affected by changing levels of nitrogen (N) than others, addition of 1 g of phosphorus (P) promotes the growth of up to 100 g algae, which represents the principal trigger of eutrophication and toxic blue-green algae blooms (Drizo, 2012). Wastewater is a main source of such contaminants thus wastewater treatment process is crucial in order to reduce the environmental impact.

* *Corresponding author*. Tel.: +46 87908609; fax: +46 84110775.
E-mail addresses: chanils@kth.se, nilsson_charlotte@live.se (C. Nilsson), ramnathl@kth.se (R. Lakshmanan), gunno@kth.se (G. Renman), gkr@kth.se (G.K. Rajarao).
[1] Tel.: +46 87906350; fax: +46 84110775.

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Approximately one-third of the population of North America uses a decentralised wastewater treatment system (US EPA, 2012) and they are also common in rural areas of Northern Europe. For instance, such systems serve about 10% of the Swedish population. Among onsite wastewater treatment systems (OWTS), the soil treatment system (STS) is frequently applied. The soil used in STS in Sweden has been recorded as having an overall low capacity for P removal from wastewater (Eveborn et al., 2012). Research by Robertson (1995) and Zurawsky et al. (2004) in Canada indicated leaching of P from septic system infiltration beds to groundwater.

Despite the alarming extent of eutrophication world-wide (WRI, 2012), to date it is mainly N removal from residential wastewater that has been regulated, and that only in the developed world. As a consequence, in the past decade a number of N removal systems have been developed and are readily available on the market. These include traditional sand recirculating systems, or newly developed systems such as Advantex, BioNest, EazyTreat, Orenco, SeptiTech, in North America (A. Drizo, pers.comm. 2012). All of these systems are based on addition of oxygen to reduce organic matter (OM) and suspended solids (SS) and help conversion of ammonium to nitrate. While these systems are effective in reducing ammonium, their discharge effluents contain 8–10 mg L^{-1} total P and continue to represent a significant threat to blue-green algae proliferation and eutrophication.

Recognising the need to find a solution to P pollution, the use of reactive filter materials for P removal has in recent years become an attractive method for the treatment of onsite wastewater. Several filter materials have been investigated and suggested for full-scale application (see reviews by Johansson Westholm, 2006; Vohla et al., 2011). Many other low-cost materials such as steel slag, bottom ash, biosorbent prepared from algae, waste tire rubber and carbon nanotubes have been suggested as adsorbents for wastewater (Jain et al., 2003; Mittal et al., 2008, 2009, 2010a, 2010b; Gupta et al., 2009, 2010, 2011a, 2011b). Mineral-based sorbents can be incorporated into a STS or used in compact filter systems, where the latter design allows for easy replacement of material and reuse of the spent material in agriculture (Renman and Renman, 2010; Cucarella et al., 2012; Drizo, 2012). On the European market, particularly in the Scandinavian countries, OWTS have also been developed for P removal systems such as Bio Cleaner, Biorock, EkoTreat, In-Drän and Topas. Some of these products use a P trap for polishing the effluent to achieve a P concentration below 1 mg L^{-1}. More importantly, regulatory frameworks that would require P removal from septic tank systems ought to be developed and enforced world-wide (Drizo, 2012).

In addition to being a major water pollutant, P is a scarce resource on a global scale (Cordell and White, 2011). Thus it is important to find efficient technologies to recover or recycle P primarily in agriculture, but also in forestry, horticulture and acid mine drainage water (Drizo, 2012). Besides the P pollution, inadequately designed or malfunctioning OWTS pose a threat as bacteria, viruses and organic contaminants (OC) can reach the recipient waters (Vega et al., 2003; Lapworth et al., 2012; O'Luanaigh et al., 2012). People can thereby be exposed to faecal human pathogens, particularly in rural areas where the water supply is mainly groundwater (Jacks et al., 2000). In order to monitor possible contamination by intestinal pathogens originating from wastewater, water samples are analysed for indicator organisms. According to the National Food Agency in Sweden (2012), the main organisms used to detect water contamination by sewage are *Escherichia coli* and intestinal Enterococci. Several studies have shown excellent removal rates of indicator bacteria in reactive filter materials used for wastewater treatment (Renman et al., 2004; Jenssen et al., 2010).

Renman and co-workers have developed a P removal technology based on the natural calcium-silicate material opoka and have tested it in Sweden and Poland (Brogowski and Renman, 2004; Renman and Renman, 2010). The calcinated product from opoka is called Polonite and systems employing this material have an elevated effluent pH, which may be detrimental to some recipient waters. Due to the alkaline nature of most reactive filter materials, the effluent wastewater may have a pH ranging between 9 and 12. These high pH values can significantly reduce microorganisms to low numbers (Heistad et al., 2006). This pH effect on bacteria reduction represents a major advantage in preventing the spread of pathogens from wastewater in the environment. On the other hand, if the recipient is a small water body, the high pH can pose a risk to the aquatic fauna; the same risk applies for ammonia, which is present in high concentrations in septic tank effluent. However, several studies have demonstrated nitrification of ammonia as well as removal of total inorganic nitrogen in reactive materials (Heistad et al., 2006; Renman et al., 2008). Moreover, the removal of organic matter is of major concern to avoid oxygen deficiency in recipient waters. Therefore a new material, Sorbulite, has been developed by this group of researchers with the aim of having lower pH in the effluent and also achieving a reduction in other pollutants such as nitrogen, organic matter and bacteria.

Therefore, the aim of the present study was to: (i) Test the novel material Sorbulite for the first time and compare its efficiency in P removal with that of Polonite; (ii) investigate the removal efficiency of faecal microorganisms by using indicator bacteria; and (iii) evaluate nitrogen and organic matter removal in the sorption and filtration process.

2. Materials and methods

2.1. Materials

2.1.1. Filter materials – chemical and physical properties

Two filter materials were used for the investigation, Sorbulite and Polonite. Polonite is a commercial product (www.bioptech.se) derived from the siliceous sedimentary rock opoka after calcination, thereby enhancing its reactivity (Renman and Renman, 2010). Sorbulite is a brand owned by Bioptech AB, Sweden, and is produced from scrap material from the manufacture of autoclaved aerated concrete (AAC). The physical and chemical properties of the materials are presented in Table 1.

2.1.2. Wastewater – chemical composition

In order to simulate the worst possible conditions for operation of a bed filter, this study used septic tank effluent

Table 1 – Chemical and physical properties of Sorbulite and Polonite.

	Sorbulite	Polonite
Si (g kg^{-1})	232	241
Al (g kg^{-1})	10.0	27
Ca (g kg^{-1})	194	245
Fe (g kg^{-1})	8.2	16.5
K (g kg^{-1})	–	9.15
Mg (g kg^{-1})	–	4.4
Mn (g kg^{-1})	–	0.12
Na (g kg^{-1})	–	1.46
P (g kg^{-1})	–	0.34
pH	9.1	13.4
Specific surface area (m^2 g^{-1})[a]	30	14
Particle size (mm)	2–4	2–6
Porosity (%)	65	45

a Measured on particle size 2 mm with the Brunauer–Emmett–-Teller (BET) method on Flow-Sorb 2300 instrument.

without any further treatment than removal of coarse, visible particles.

The wastewater used in the experiment was collected in plastic containers on five occasions from two different sedimentation tanks used for the treatment of wastewater serving one and four households, respectively. Average values for the composition of the wastewater used are given in Table 2.

2.2. Methods

2.2.1. Column experiment

The experiment was performed using a recirculation system, see Fig. 1. Three replicate columns (height 20 cm and diameter 5.5 cm) were used for each filter material studied. The columns were packed to a height of about 17 cm. Each column was fed with wastewater from individual glass bottles (volume of 1 L). The wastewater was pumped through the columns in a continuous up-flow direction (5 mL min^{-1}) and the effluents were recirculated back to the containers. The column experiment was performed in the laboratory at room temperature (20 °C). All of the columns were covered with aluminium foil in order to protect the material from being affected by light during the experiment.

The experiment lasted for 90 days, excluding short breaks when hoses and wastewater were changed. The total volume of wastewater used for each column was 47 L, i.e. 47 batches.

Table 2 – Composition of the wastewater used in the column experiment. Values are averages for the different batches used; standard deviations are given in brackets.

Parameter	Mean (±SD)
pH	7.39 (0.53)
Total inorganic nitrogen (TIN, mg L^{-1})	78.82 (35.5)
Phosphate-phosphorus (mg L^{-1})[a]	8.95 (4.13)
Total organic carbon (TOC, mg L^{-1})	30.61 (10.39)
E. coli (CFU 100 mL^{-1})	$1.05 \cdot 10^5$
Enterococci (CFU 100 mL^{-1})	$2.2 \cdot 10^5$

a Wastewater dominated by PO_4–P (85%).

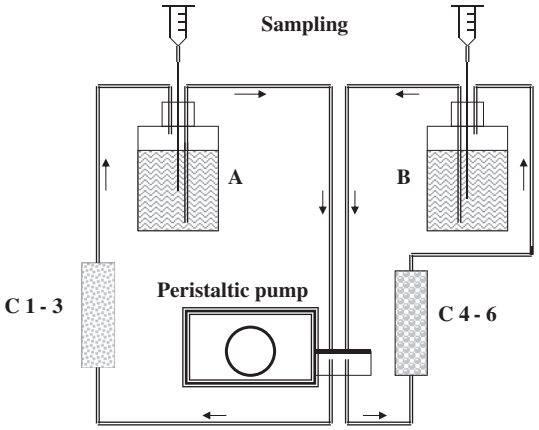

Fig. 1 – Schematic presentation of the experimental set-up. Columns filled with Polonite (C1-3) and Sorbulite (C4-6) were filled with wastewater from individual bottles filled with wastewater, to which the effluent was recirculated back after passed through the columns.

However the volume passing through each of the columns due to the recirculating mode, ranged between 644 and 652 L. The operating parameters for the columns are given in Table 3. The voids hydraulic retention time (HRT) for each of the columns was determined by triplicate measurements as shown in Equation (1).

$$HRT = \frac{V}{Q} \quad (1)$$

where V is volume of liquid pumped and Q is the flow rate.

The mean values for each of the columns ranged between 0.48 and 0.67 h. The mean number of recirculated pore volumes (PV) per day was 44 for Polonite columns and 37 for Sorbulite columns. The unusually high hydraulic load was used as a mean to exhaust the filter materials with regards to their phosphorus sorption capacities.

2.3. Sampling and analysis

Sampling and analysis were carried out on a batch basis. Prior to the change of wastewater, samples were taken for analysis, after which the water was discharged and replaced. The steady state concentration for P (as PO_4–P) in sorbed or liquid state was determined in kinetic studies parallel to the experiment. This was done by allowing each volume of water to pass through the column system until chemical analysis showed that further sorption of P to the filter material did not appear. On the basis of the data obtained, the wastewater in the bottles was changed after 24 h, 48 h and 72 h. Measurements of pH using a pH meter of model PHM 95, Radiometer, Copenhagen, as well as analysis of phosphate (PO_4–P) was performed on all samples, whereas total inorganic nitrogen (TIN), total organic carbon (TOC) and bacteria were analysed on samples from batches 1–9, 28–31 and 43–47. All measurements and analyses were performed at room temperature, with measurement of pH and analysis of TOC and bacteria performed on unfiltered samples. The mean

Table 3 – Operational parameters for the column experiment, retention times are calculated as the ratio of the saturated pore volume to total flow through the column.

Column	Mass of material, dry weight (g)	Bed volume (BV, cm^3)	Pore volume (PV, cm^3)	Retention time/ cycle (HRTv, h)	Total treatment	
					PV (n)	Vol. (L)
C1 Polonite	300	420	144	0.48	4469	644
C2	300	410	170	0.57	3812	648
C3	301	425	176	0.58	3703	652
C4 Sorbulite	124	410	196	0.65	3323	651
C5	116	430	200	0.67	3240	648
C6	116	420	184	0.62	3503	645

percentage reduction in bacteria (R_b), the mean reduction in TOC (R_C) and TIN (R_N) removal were calculated using Equation (2).

$$R_b,\ R_C,\ R_N = \left(\frac{C_i - C_e}{C_i}\right)\cdot 100 \quad (2)$$

where C_i and C_e denote the concentration of the parameter analysed in the influent and effluent waters, respectively.

2.3.1. *Phosphate and nitrogen analysis*

Samples were filtered through a 0.45 μm Sartorius filter prior to analysis of P in the form of phosphate (PO_4–P) and inorganic species of nitrogen, i.e. nitrite, nitrate and ammonium (NO_2–N, NO_3–N and NH_4–N). This analysis was performed using Flow Injection Analysis (FIA, Aquatec-Tecator, Sweden). The instrument was calibrated prior to analysis, using standard solutions with a concentration of 100 mg L^{-1} of the element to be analysed.

2.3.2. *Carbon analysis*

Measurement of TOC was performed according to APHA et al. (1995). The TOC was estimated by measuring total carbon (TC) and inorganic carbon (IC) and then calculated as the difference between TC and IC using TOC-5000 instrument, Shimazdu Corporation, Japan. The instrument was calibrated prior to analysis using standard solutions with a concentration of 100 mg L^{-1} of organic and inorganic carbon, respectively.

2.3.3. *Microbial analysis*

The colony forming units (CFU mL^{-1}) of *E. coli* and Enterococci were calculated before and after treatment of wastewater through the Polonite and Sorbulite materials from the selected batches. The samples were collected after each batch and stored at 4 °C until analysis. As selective medium, EMB agar plates were used for *E. coli* and Bile Esculin agar plates for Enterococci according to APHA et al. (1995). The plates were incubated for a period of 24–48 h and the number of CFU mL^{-1} was calculated on each plate. Triplicate plates were analysed for all samples and the mean count for these triplicates was recorded. All reagents were procured from Sigma–Aldrich and were of analytical grade.

2.3.4. *Data analysis*

After analysis, the percentage cumulative phosphate removal (cpr) for each of the batches and columns was calculated according to Equation (3).

$$\mathrm{cpr_r} = \left(1 - \left(\frac{\sum_1^n P_e}{\sum_1^n P_i}\right)\right)\cdot 100 \quad (3)$$

where n is the number of batches and P_e and P_i denote the phosphate concentrations in the effluent and influent water, respectively.

Data on cumulative P removal and pH values for the two materials were statistically tested for outliers using Grubb's test ($p < 0.05$) (GraphPad, 2012), and any outliers detected were removed. Thereafter, the mean cumulative phosphate removal for each batch and material was calculated from the values obtained for all three replicates for that specific batch and material.

Univariate Analysis of Variance and regression analysis were used to test for differences in pH and P removal between the filter materials. One-way ANOVA was used to compare the performance of the individual columns in order to determine any significant differences between the replicates. Furthermore, the TOC removal and bacteria reduction in the materials was analysed using one-way ANOVA in order to compare the mean removal and reduction in the two materials and regression analysis was used to examine changes in the removal and reduction over time. All statistical analyses were performed using the statistical software SPSS Statistics 19 (IBM, 2012).

3. Results and discussion

3.1. *pH and phosphate removal*

Cumulative PO_4–P reduction and change in pH over time in the filter materials are shown in Fig. 2. The cumulative removal in Polonite decreased from 100% and remained at 80%. The amount of sorbed PO_4–P was calculated to be 1.14 mg g^{-1} Polonite and the mean removal of the total load was 80.9%. The pH decrease from 13.4 to 7.9 observed in the Polonite columns corresponds to the decrease in phosphate reduction observed by Gustafsson et al. (2008) and Renman and Renman (2010). The cumulative PO_4–P removal by Sorbulite decreased from 90 to 75%, with a mean removal of 74.9% of the PO_4–P loaded, and the amount of sorbed PO_4–P was calculated to be 2.64 mg g^{-1}. The pH in columns filled with Sorbulite decreased from 9.1 to 8.9. This low decrease in pH is consistent with findings by Renman and Renman (2012). Furthermore, the positive correlation between pH and PO_4–P reduction in both materials was confirmed using linear

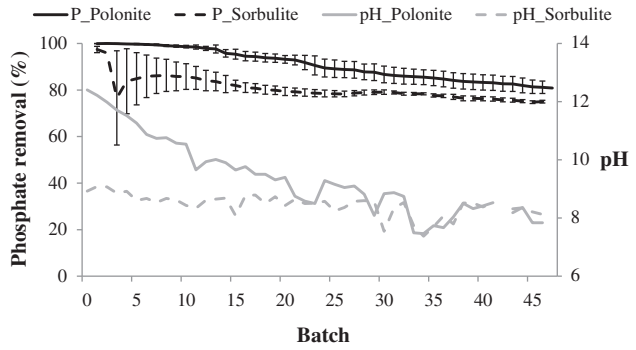

Fig. 2 – Change in pH over time and average cumulative removal of phosphate in Polonite (Polo) and Sorbulite (Sorb). Standard deviations indicated with vertical bars.

regression and univariate analysis of variance ($p < 0.01$). In addition, the greater PO_4–P removal rate seen in Polonite compared with Sorbulite was confirmed using one-way ANOVA and linear regression ($p < 0.01$). This is also evident from the breakthrough curves (Fig. 3), which show a consistently higher removal of phosphate in Polonite. Even though the percentage removal of phosphate was higher in Polonite as compared to Sorbulite, the amount of phosphate sorbed to the materials using mass-balance calculations was higher in the Sorbulite material. This is most likely due to the higher porosity and specific surface area of this material. A comparison of the phosphate removal efficiency of different mineral-based sorbents is shown in Table 4. The amount of PO_4–P removed by Polonite in the present study was much lower compared to the maximum sorption capacity of 119 mg g^{-1} reported by Brogowski and Renman (2004). However, that study used material with a particle size of 0–0.5 mm, thereby resulting in a much larger specific surface area as compared to the fraction size used in the present study. Since Sorbulite is a fairly new material, there are few previous studies using this material. Oğuz et al. (2003) reported phosphate removal ratios of 99% using gas concrete (i.e. raw material for production of Sorbulite) in adsorption experiments. Furthermore, according to Renman and Renman (2012), Sorbulite has a very high P removal of 39.6 mg g^{-1}, as determined in a box experiment where the HRT was 30 h.

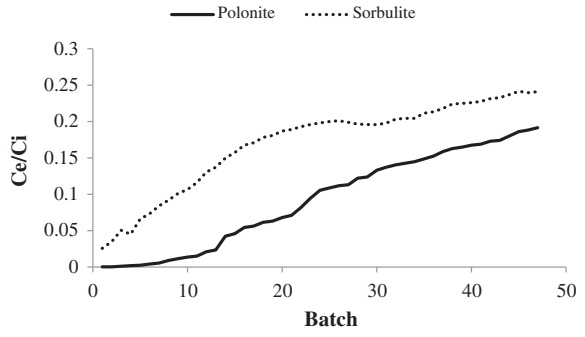

Fig. 3 – Breakthrough curves for phosphate removal over time in Polonite and Sorbulite columns. The Ce/Ci values represents the ratio between phosphate concentration in effluent (Ce) and influent (Ci).

Based on Langmuir isotherms, those authors reported a sorption capacity (PSC) of 28 mg g^{-1} using wastewater. The higher calculated amount of phosphate sorbed to Sorbulite as compared to Polonite seen in the present study, in combination with the lower pH of this material, makes it an attractive candidate for future research on recycling of phosphorus.

Our kinetic study showed that Sorbulite needs a contact time, i.e. a re-circulating time of more than 24 h to approach 100% P removal and that this time increases when the material is ageing. Polonite has a much better reactivity but its P removal capacity drops much faster with time. The equilibrium data fitted the Langmuir isotherm equation better than the Freundlich equation for both sorbents (data not shown). The best fit of equilibrium data in the Langmuir isotherm expression predicted mono-layer coverage of P onto the Sorbulite and Polonite surface. It was found that the pseudo-second order rate constants decreased with increasing initial concentrations (data not shown). The fitted and the experimental values were very close to each other. In the view of these results, it can be said that the pseudo-second order kinetic model provided a good correlation for the adsorption of P onto Sorbulite and Polonite, in contrast to the pseudo-first order model. Sorbulite is a hard structure, built by the presence of tobermorite. However this calcium silicate hydrate triggers kinetically inhibited formation of calcium phosphate compounds. Polonite, on the other hand, with its very high initial pH and dissolved Ca, is able to precipitate PO_4^{3-} quantitatively as calcium phosphates (Gustafsson et al., 2008). The effect of particle size on adsorption in porous materials has been observed in several investigations. A study by Jain et al. (2003) indicated that adsorption capacity increases to some extent with the decrease in particle size of the sorbent. For the Polonite investigated here it is suggested that the access to all pores is facilitated as particle size becomes smaller.

In the light of the high hydraulic loading and very short HRT used in the present study, it is reasonable to expect lower phosphorus removal compared with that reported in previous studies. The steadily decreasing P concentration in the re-circulated wastewater of each batch might have favoured desorption rather than sorption. A volume of 47 L of wastewater was treated in a bed volume of about only 420 cm^3. In a full-scale filter system with Polonite used in Sweden, a volume of 700 L is designed to treat the wastewater from one household during 2 years at most. Based on the data in our study, this design volume would be able to treat 78 m^3 of wastewater with 81% removal efficiency. However the surface load in the column experiment was as high as about 3000 L m^2 d^{-1}, compared with the design value for Polonite filters of 700 L m^2 d^{-1}. This "acid" test demonstrates the high P removal performance of Polonite and the capacity of the new material, Sorbulite. However the latter has a slower release of Ca^{2+} ions, which depends on its mineralogy, i.e. the presence of tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) (Renman and Renman, 2012). The column test adopted here with recirculating wastewater limited dissolution of atmospheric CO_2 in the water, as it is a closed system, compared with columns operated with continuous flow of wastewater. It is known that CO_2 is an inhibitor of P precipitation (Valsami-Jones, 2001). Therefore a reactive filter would be exhausted much faster if more CO_2 were available, which would be the case with less pre-treated wastewater.

Table 4 – Comparison of various mineral-based sorbents and their removal efficiency of phosphate and nitrogen species from aqueous solutions.

Sorbent	Experiment		Particle size (mm)	Removal capacity (mg g^{-1})		Reference
	Batch	Column/box		Phosphate	Nitrogen	
Filtralite P	X[a]		0.5–4	2.5	–	Ádám et al., 2007
Shellsand	X[a]		3–7	9.6	–	Ádám et al., 2007
Turkish zeolite	X[b]		1–2	–	1.32 (NH_4^+)	Sarioglu, 2005
CAAC/Sorbulite	X[a]	X[b]	2–4	57/39.6	–	Renman and Renman, 2012
Polonite		X[b]	2–5.6	1.30	1.42 (TN)	Renman and Renman, 2010; Renman et al., 2008
Polonite		X[a]	0–0.5	119	–	Brogowski and Renman, 2004
Polonite		X[b]	2–6	1.14	1.32 (TIN)	This study
Sorbulite		X[b]	2–4	2.64	6.68	This study

a Synthetic wastewater/solution.
b Domestic wastewater, TN Total nitrogen, TIN Total inorganic nitrogen.

The effect of organic matter on phosphate reduction in filter materials is not clearly understood. Bird and Drizo (2010) reported a decrease in phosphate removal in slag due to increased total suspended solids and Nilsson (2012) reported increased phosphate removal in Polonite and slag material with a decreased concentration of BOD. Renman and Renman (2010) reported similar removal efficiency in Polonite using synthetic solution and wastewater, although this was ascribed to a lower loading rate when using wastewater. On the other hand, Ádám et al. (2007) did not observe any significant differences in P retention in Filtralite P when using a synthetic solution and wastewater. Barca et al. (2012) reported higher phosphate removal in slag when using wastewater compared with synthetic solution.

3.2. *Total inorganic nitrogen removal*

The reduction in total inorganic nitrogen (TIN) in Polonite and Sorbulite is shown in Fig. 4a (batch 1–9) and 4b (batches 28–31 and 43–47).

In the initial period (batch 1–9), the average removal of TIN in Polonite was 8%, while in the middle (batch 28–31) and final (batch 43–47) period it was 5 and 21%, respectively. The corresponding values for Sorbulite were 21% in the initial period, 17% in the middle period and 31% in the final period. The total average removal of TIN in Polonite and Sorbulite was 11% and 23%, respectively. Jenssen et al. (2010) showed removal rates of TIN ranging from 32 to 66% in filter beds with Filtralite treating domestic wastewater. Renman et al. (2008) found a removal rate of 17.7% in Polonite filters used for wastewater treatment. A comparison of the nitrogen removal efficiency of different mineral-based sorbents is shown in Table 4. As seen from the table the TIN removal rates of 11% (Polonite) and 23% (Sorbulite) in this study corresponds to removal capacities of 1.32 mg g^{-1} and 6.68 mg g^{-1} in Polonite and Sorbulite respectively. The higher difference between the two materials seen in the removal capacities as compared to the percentage removal rates is related to the 2.5 times higher density in Polonite compared to Sorbulite.

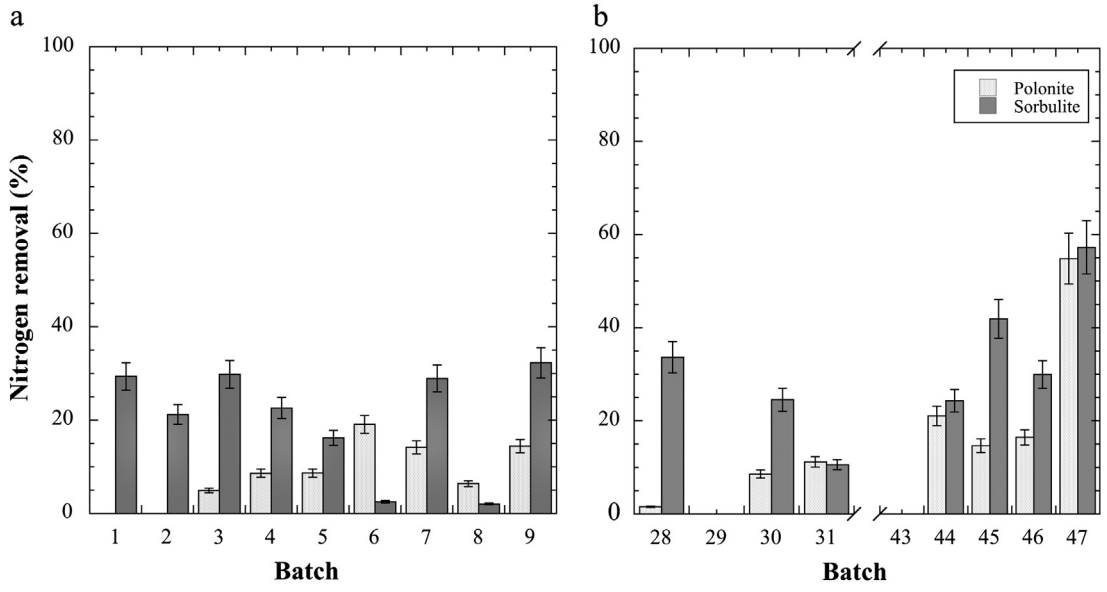

Fig. 4 – Percentage removal of total inorganic nitrogen (TIN) in Polonite and Sorbulite for (a) batches 1–9 and (b) batches 28–31 and 43–47.

Initially, when the column pH was above 10 most of the nitrogen was in the form of ammonium and it is very unlikely for nitrification or denitrification processes to take place. As the pH reduced gradually and the column material stabilized, nitrification and denitrification might have been initiated. This is supported by the approximate effluent concentrations of nitrate and nitrite of 40 mg L^{-1} and 50 mg L^{-1} respectively (data not shown). Sorbulite effluent had lower nitrate concentration compared to Polonite at batch 43 and more nitrite was released at batches 44–46. At these points the ammonium level was very low compared to the initial batches (1–9) indicating that at higher pH, most of the nitrogen was in the form of ammonium, which would enable precipitation with P. Booker et al. (1999) reported that the maximum amount of ammonium removal and P removal was at pH 9.2 and 9.8 respectively. The nitrogen removal depends on pH, temperature, retention time, redox status and wastewater characteristics. The drop in pH could be due to the nitrification process as can be observed in both materials used in the present study.

Furthermore, the porous structure of Sorbulite, in combination with its lower pH compared to Polonite, would provide better conditions for bacterial growth and the formation of a larger, more dispersed biofilm. Therefore, the reduction in TIN was controlled by the pH and surface area of the material, as well as the bacteria attached in the column.

3.3. TOC removal

The removal of total organic carbon in Polonite and Sorbulite is shown in Fig. 5a (batch 1–9) and 5b (batches 28–31 and 43–47). The average removal of TOC in Polonite was −72% for the initial period, whereas for the middle and final period it was 2 and -79%, respectively. For Sorbulite, the corresponding values were 45, 4 and −99% in the initial, middle and final periods respectively. The average removal in TOC was −51% in Polonite and −1% in Sorbulite. One-way ANOVA showed no significant differences between the two filter materials with respect to TOC removal ($p = 0.127$), but regression analysis showed that the overall TOC removal decreased over time ($p < 0.05$).

In the present study, the TOC removal in Polonite (Fig. 5) fluctuated throughout the experiment, without any clear pattern. When Sorbulite was used as the filter material, on the other hand, the removal was positive in the first part of the experiment (Fig. 5a) and decreased with time to negative values at the end of the experiment (Fig. 5b). This pattern is consistent with the conclusion drawn by Song et al. (2006) that the removal of humic substances increases with increasing pH. Furthermore, based on the higher porosity in Sorbulite than in Polonite, the possibility of straining is greater in the former, thus favouring greater removal of organic carbon (McDowell-Boyer et al., 1986). Wendling et al. (2012) reported release of DOC in sand columns and attributed this to the loosely bound organic matter from packing as well as from breakdown of organic matter inside the columns. The negative TOC removal in the present study might be explained by similar releases of organic material from the wastewater and from dead bacteria. After each flush-out, new organic material presumably accumulated in the material until it was flushed out again.

3.4. Bacteria reduction

The reduction in *E. coli* and Enterococci in the two filter materials is shown in Figs. 6 and 7, respectively.

The reduction in *E. coli* in Polonite was on average 76% in the initial period, 65% in the middle periods and 25% in the final period (Fig. 6). In Sorbulite, the mean reduction rates were 73, 24 and 12% in the initial, middle and final periods, respectively. The reduction in Enterococci (Fig. 7) in Polonite was 75, 59 and 18% in the initial, middle and final period, whereas in Sorbulite it was 56, 20 and 7% respectively. The total average reduction in *E. coli* was 60% in Polonite and 45% in Sorbulite, while for Enterococci the corresponding value was 56% in Polonite and 34% in Sorbulite. There was thus an evident difference in microbial reduction between the two

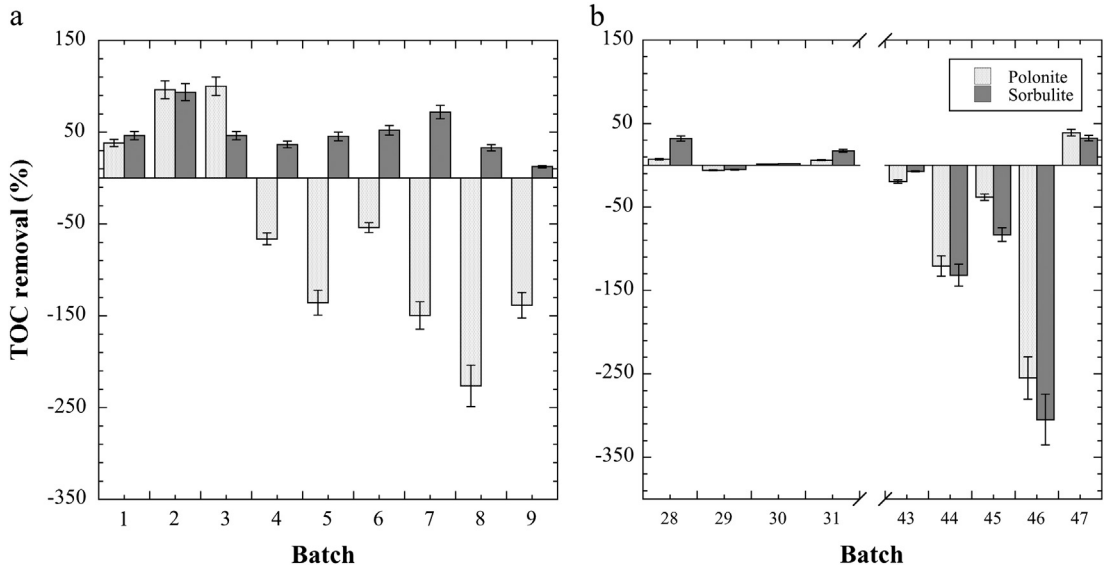

Fig. 5 – Percentage removal in TOC in Polonite and Sorbulite for (a) batches 1–9 and (b) batches 28–31 and 43–47.

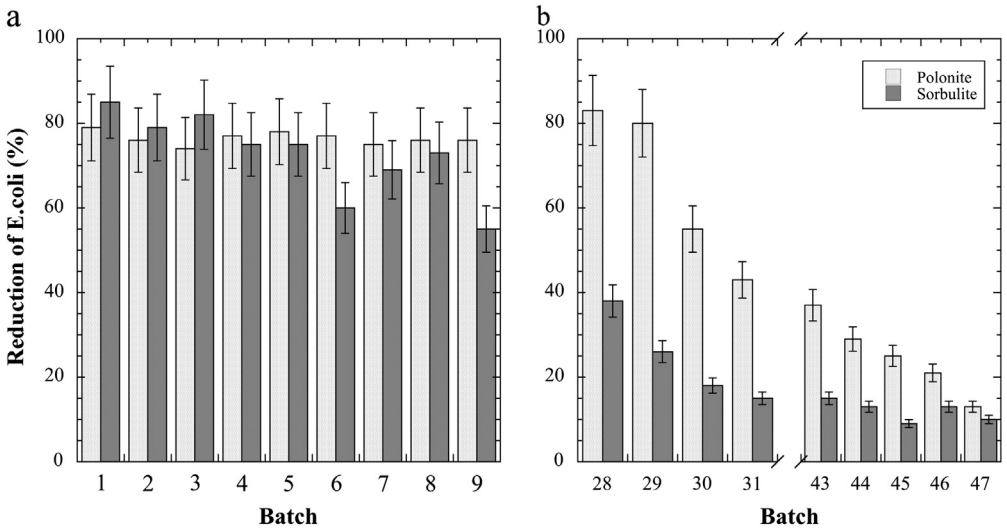

Fig. 6 – Percentage reduction in *E. coli* in Polonite and Sorbulite for (a) batches 1–9 and (b) batches 28–31 and 43–47.

materials, with Polonite showing a higher reduction rate of Enterococci and *E. coli* over a longer time than Sorbulite. The removal efficiency of both Polonite and Sorbulite decreased with time, leading to increased numbers of Enterococci and *E. coli* in the effluent. Both filter materials had almost reached breakthrough by the end of the experiment, removing approximately 15% of *E. coli* and 10% of Enterococci.

The mechanisms involved in the immobilization of pathogens in wastewater are straining and adsorption (Stevik et al., 2004). Straining is determined by the size of the material and the bacterial cells. According to Corapcioglu and Haridas (1984), larger cells are removed effectively by filtration, whereas smaller cells can penetrate deeper into the material. Furthermore, straining is also affected by clogging, a common process causing accumulation of stable solid materials between particles or on the surface of the material. The growth of microorganisms and excretion of extracellular polymeric substances (EPS) from bacteria also lead to accumulation of biomass on the material, thereby causing decreased permeability of the filter and increased retention (McDowell-Boyer et al., 1986).

In the present study, straining might have been important regarding microbial reduction in the clogging zones of the materials, whereas in other parts of the filters adsorption was the more probable mechanism. Adsorption is dependent on immobilisation by bacteria, which in turn is determined by the contact time (Stevik et al., 2004). Ausland et al. (2002) reported increased removal of coliform bacteria using uniform pressure distribution and retention times. According to Stevik et al. (2004), organic matter can decrease bacteria sorption by blocking sorption sites on the material. It is also possible that charged organic matter affects the charge of the column material, thereby affecting the attractive and repulsive interactions between bacteria and filter material. On the other hand, organic matter can increase the surface area of the material and thereby also the number of adsorption sites for

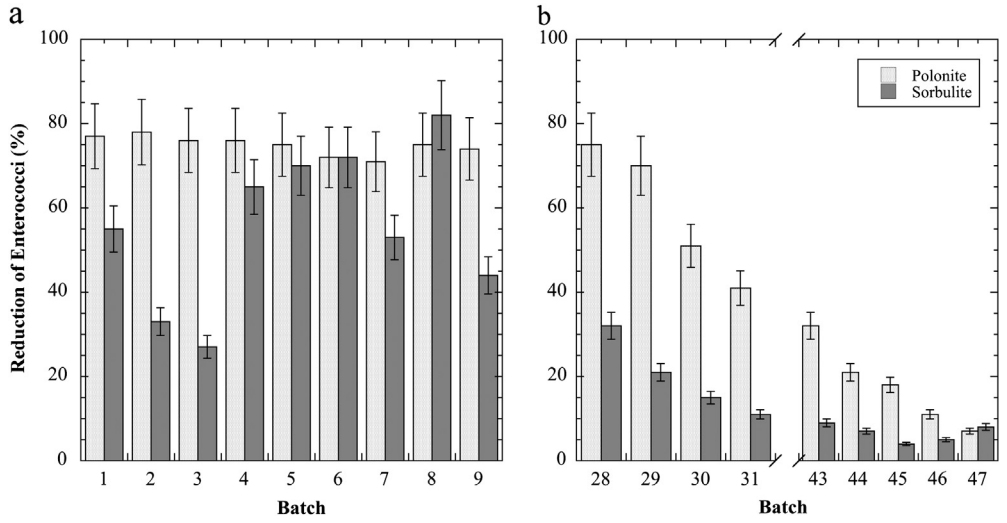

Fig. 7 – Percentage reduction in Enterococci in Polonite and Sorbulite for (a) batches 1–9 and (b) batches 28–31 and 43–47.

bacteria. The effect of organic matter and reduction of bacteria was investigated by Nilsson (2012), by comparing the increase in bacteria removal with increasing concentration of BOD.

The bacteria reduction observed in the present study was lower than that in previous studies using Polonite as a filter material (Renman et al., 2004). The total average amount of bacteria remaining in the treated water, as compared to the influent water (Table 2), for *E. coli* was 42 CFU mL^{-1} in Polonite and $5.7 \cdot 10^2$ CFU mL^{-1} in Sorbulite, while for Enterococci the corresponding value was 97 CFU mL^{-1} and $1.4 \cdot 10^2$ CFU mL^{-1} in Polonite and Sorbulite respectively. One possible reason for these differences is the recirculating system used in the present study and the very high hydraulic load. By recirculating the water back to the influent, the concentration of bacteria in the incoming water would decrease. Since adsorption of bacteria is dependent on the bacteria concentration (Stevik et al., 2004), this in turn would result in reduced removal rate. The decrease in reduction seen in Polonite from batch 29 coincided with the pH falling below 9, whereas in Sorbulite, on the other hand, the pH was consistently lower. Based on this difference in pH as well as the more porous structure of Sorbulite, it can be concluded that the bacteria reduction in Sorbulite is mostly dependent on straining in the smaller pores of the material, probably facilitated by clogging due to accumulation of organic matter. The bacteria reduction seen in Polonite initially can be attributed to high pH, followed by straining in smaller pores created by clogging.

3.5. *Hydraulic performance and removal patterns*

The two materials were tested by applying batches of wastewater with high hydraulic loading (5 mL min^{-1}) and short retention time (average 36 min) until phosphate equilibrium was achieved.

It should be borne in mind that the overall fluctuations observed in the removal of PO_4–P, TOC and bacteria by Polonite and Sorbulite could be due to numerous reasons. Packing of the columns was performed identically, but the columns were still likely to have differed since the distribution of pores and channels can vary and cause differences in available sorption sites. Moreover, throughout the experiment smaller channels and pores could have become clogged (McDowell-Boyer et al., 1986), thereby decreasing the differences as well as causing fluctuations in PO_4–P removal, as observed for the Sorbulite (Fig. 2). In contrast, Polonite demonstrated increased fluctuations with time, which was probably related to losses of organic matter from the matrix.

4. Conclusions

Two filter materials, Polonite and Sorbulite, were compared with respect to their capacity for removal of phosphate, total nitrogen, total organic carbon and indicator organisms from wastewater. The study was based on a new test methodology, involving a circulatory column system. The results demonstrated that Polonite was superior to Sorbulite in removal of phosphate and bacteria, which can be attributed to the dissolution of CaO in Polonite and its high pH. Sorbulite performed better with regard to removal of total nitrogen and total organic carbon, which can be attributed to its higher porosity and lower pH, resulting in better conditions for retention of organic matter and bacteria and thereby possibly also for denitrification. The methodology used resulted in lower removal rates of phosphorus, total organic carbon and bacteria owing to the recirculation treatment process and high surface loading. However the results demonstrated high phosphorus removal efficiency of the materials investigated, as well as possible removal of nitrogen, thereby providing superior performance of the material in wastewater treatment process.

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